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14. ABSTRACT
The focus of this project was to acquire and use computer cluster nodes purchased with AFOSR DURIP funding for the multiscale simulation of ionic liquids and the construction of a novel molecular design methodology. During the funding period atomistic and coarse-grained (CG) molecular dynamics (MD) simulations of ionic liquids were performed to study the structure and dynamical properties of the ionic liquids. An effective force coarse graining (EF-CG) method was developed to build transferable CG models, and a systematic inverse coarse-graining molecular design approach was developed based on the EF-CG model and an empirical CG-structure-property relationship.

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A) Objectives

Objectives of original proposal were met and the results are outlined in this final report.

B) Status of Effort for Duration of Funding

The focus of this project was to acquire and use computer cluster nodes purchased with AFOSR DURIP funding for the multiscale simulation of ionic liquids and the construction of a novel molecular design methodology. During the funding period atomistic and coarse-grained (CG) molecular dynamics (MD) simulations of ionic liquids were performed to study the structure and dynamical properties of the ionic liquids. An effective force coarse graining (EF-CG) method was developed to build transferable CG models, and a systematic inverse coarse-graining molecular design approach was developed based on the EF-CG model and an empirical CG-structure-property relationship.

C) Significant Work Accomplished

The behavior of the ionic liquid/vacuum interface was studied by applying the multi-scale coarse-graining (MS-CG)[2-4] method,[5], and the MSCG models of 1-alkyl-3-mehtylimidazolium-based ionic liquids (IL) with alkyl substituent of different lengths were developed. When the chain length of cations increases, a monolayer ordering will change to a unique multilayer ordering and the surface tension will decrease and approaches a constant, consistent with Langmuir theory[6] and experiments.[7, 8] A detailed orientational study demonstrated that the alkyl chain of cations prefers to align parallel to the surface normal while the aromatic ring tends to be perpendicular to the surface normal. The surface electron density profile shows that the surface electron density oscillations are mainly contributed by cations. Figure 1 (a) through (d) (shown at right) illustrates the 1-dodecyl-3-methylimidazolium/NO_3^- system, revealing a clear multilayer ordering: (a) all CG sites; (b) CG sites of aromatic rings, the CH_3 groups on long side chains and anions; (c) CG sites of the CH_3 groups on long side chains; and (d) CG sites of aromatic rings and anions.

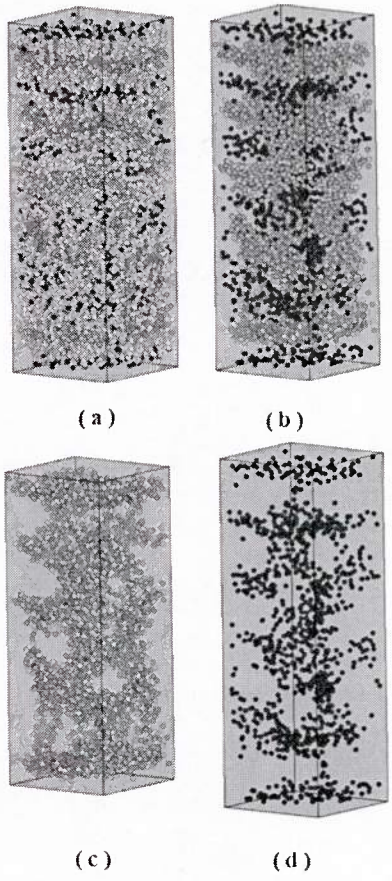

Figure 1[5]

An effective force coarse-graining (EF-CG) method was developed to build transferable coarse-graining force field[1]. In the EF-CG method, the effective pairwise forces between coarse-grained sites were calculated by taking the average of the atomistic forces between the corresponding atomic groups in configurations sampled from equilibrated atomistic molecular dynamics simulations. When compared with more general MS-CG method, the EF-CG method keeps the transferable part of the MS-CG at the cost of slightly reduced structural accuracy. Therefore, as an alternative to the

MS-CG method, the EF-CG method determines the CG force fields with higher transferability but reduced structural accuracy. The computer hardware purchased with the DURIP funding great facilitated the development and testing of the EF-CG method.

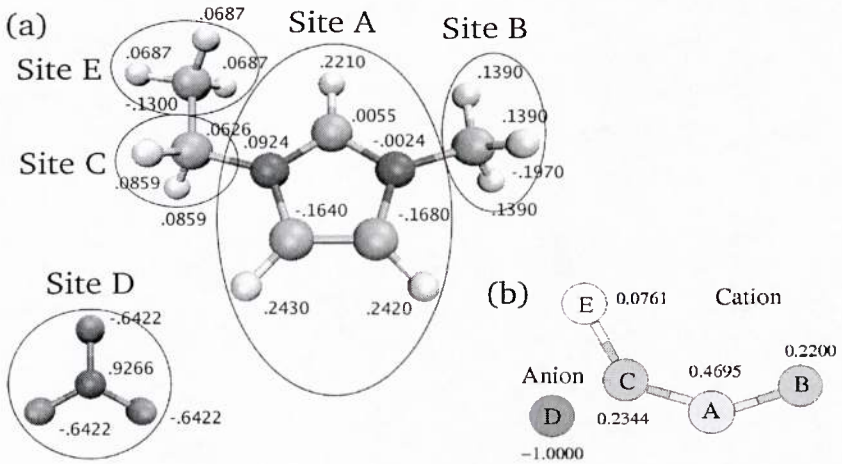

Figure 2[1]

For ionic liquid systems, the EF-CG method reproduced all liquid state structure with little loss in local structure details. In particular, the 1-ethyl-3-methylimidazolium (EMIM)/NO_3^- system was studied by using the EF-CG method. Figure 2 (shown above) (a) and (b) are the all-atom and EF-CG models for EMIM/NO_3^-. Figure 3 below shows the comparison of radial distribution functions (RDFs) for different CG sites between EF-CG and all-atom MD results.

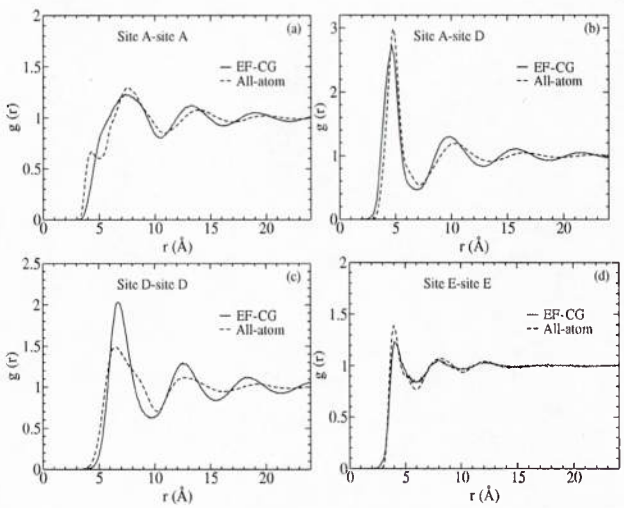

Figure 3[1]

The transferability of the EF-CG force filed was studied for different ionic liquid structures[9] and different temperatures.[1, 9] One IL was used to reproduce the structures of IL with different side chain length and the transferability of any two ionic liquids decreased when

increasing the difference between the side chain lengths of that two ionic liquids. Figure 4 (shown below) depicts selected RDFs for the 1-decyl-3-methylimidazolium/NO_3^- (C10): In Figure 4 (a) is the RDF for head groups and (b) is the RDF for tail groups. The head group is taken as the aromatic ring of the cations with the CH_3 on the long alkyl side chain as the tail group. For the black curve, the EF-CG force field was calculated from an all atom simulation of 1-octyl-3-methylimidazolium/NO_3^- (C8), and for the red curve, the EF-CG force field was calculated from an all atom simulation of a C10 system. The RDFs show very good agreement between the EF-CG force field coming from C8 and C10. Therefore, the EF-CG force field has good transferability between ILs with different side chain lengths.

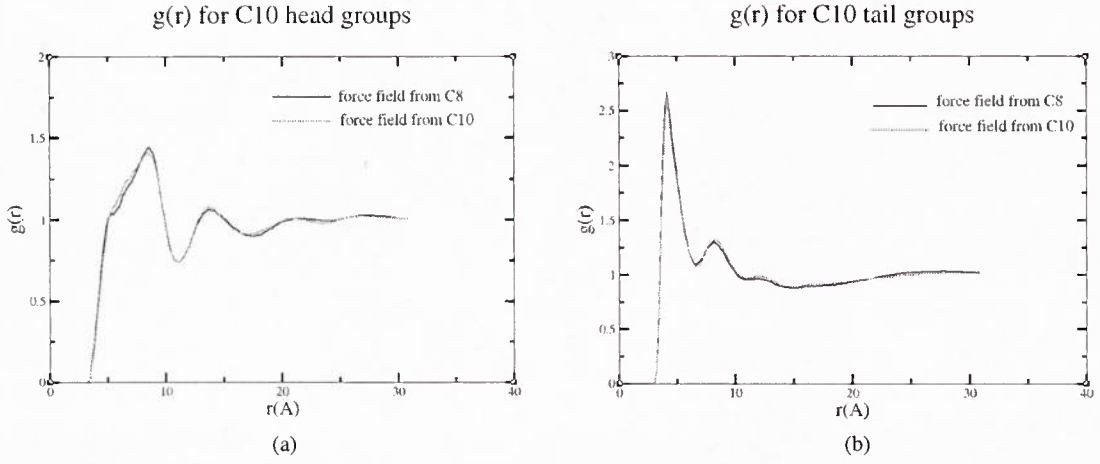

Figure 4

The EF-CG simulation, under different temperatures, revealed the EF-CG force fields have very good transferability within the temperature range studied (298K-700K).[1, 9] Figure 5 below shows the RDFs of 1-hexyl-3-methylpyridinium/PF_6^- (HMPM/PF_6^-) systems at 400K. Figure 5 (a) is for head groups and (b) is for tail groups. For the black curve, the EF-CG force field was calculated from an all-atom simulation of HMPM/PF_6^- at 298K and the EF-CG force field for the red curve was calculated from an all-atom MD simulation of HMPM/PF_6^- at 400K. The results show the very good temperature transferability of EF-CG force field.

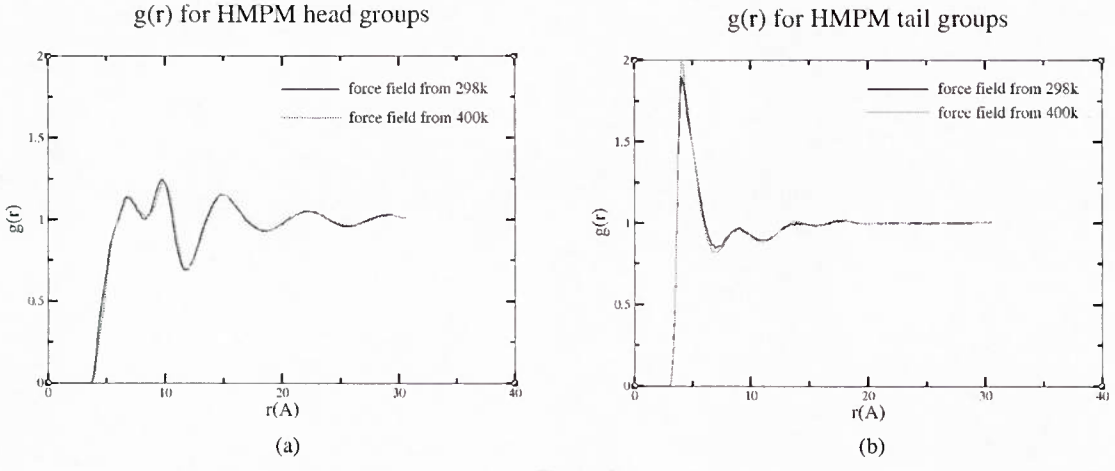

Figure 5

Based on the EF-CG method, an empirical relationship between CG structure and a desired set properties, an inverse coarse-graining (ICG) approach, has been developed with the following procedure:[9] 1) several sets of ionic liquids were selected to represent the general properties of a wide range of such liquids; 2) all atom MD simulations were carried out for each selection; 3) EF-CG models were built for each IL and the force fields for each of the CG sites were added to the EF-CG library. At the same time, an empirical CG-structure-property network was built based on the relationship between CG structures and the target properties of density and heterogeneity. Given the desired properties (i.e., density and heterogeneous order parameter [10]), the CG-structure-property network provided predicted CG structures. Next, a search of the EF-CG library was conducted to construct a proper force field for the CG structures which came from the CG-structure-property network. Finally, an EF-CG simulation was performed for the constructed CG models to choose the best CG representations followed by an all atom MD simulation with each of the CG representations, giving the best all-atom representations, which provide the final IL result for a given desired density and heterogeneous order parameter.

Description of Computational Codes

DL_POLY: http://www.csc.scitech.ac.uk/ccg/software/DL_POLY/
Gromacs: http://www.gromacs.org/
Revised DL_POLY: MD simulation package specially used to do the polarizable model calculation.
MS-CG: computational codes used to build MS-CG model based on all atom simulations
EF-CG: computational codes used to build EF-CG models based on all atom simulations

Description of the Computing Cluster Purchased with DURIP Funding

A new 384-core Dell PE 1950 rackmount server cluster, purchased with the awarded DURIP funds (FA9550-01-1-0082), was built and has been used to help fulfill the computational requirements of the research projects outlined above. The DURIP funds used to purchase this cluster equipment which included 48 compute nodes, 3 service/management nodes, a fully non-blocking Qlogic SDR InfiniBand (IB) switch, a Gigabit Ethernet (GigE) switch, and an 8-TB global scratch space. Each compute node has two 2.33/2.66 GHz quad-core Intel Xeon processors (for a total of 8 cores per node), 16 GB RAM (2 GB per core), 500 GB local disk, and an x4 SDR IB Qlogic/Pathscale "InfiniPath" single-port HCA (Host Channel Adapter) card over x8 PCI-E for very low-latency and high-bandwidth communication.

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